

11th International Conference on Modern Building Materials, Structures and Techniques,
MBMST 2013Evaluation of the Influence of Ultradisperse Dust and Carbon
Nanostructures on the Structure and Properties of Gypsum BindersAnastasiia Gordina^{a,*}, Yury Tokarev^b, Grigory Yakovlev^c, Jadvyga Keriene^d,
Stanislav Sychugov^e, Ali El Sayed Mohamed^f^{a,b,c,e}Faculty of Civil Engineering, Izhevsk State Technical University, Izhevsk, Stencheskaya St., 7, Russia^dDepartment of Chemistry and Bioengineering, Vilnius Gediminas Technical University, Vilnius, Sauletekio al., 11, Lithuania^fEgyptian-Russian University, Cairo, 87 El-Tahrir St., Egypt**Abstract**

The influence of carbon nanostructures of chemical company “Arkema” and ultradisperse metallurgical dust on the properties and structure of gypsum matrix has been studied with the help of mechanical tests, X-ray phase and microstructural analyses. The additives are introduced into the gypsum binder both separately and together. When carbon nanotubes are used in the amount of 0.001%, the ordered and dense structure is formed that results in improving mechanical properties up to 80%. The carbon nanostructures act as crystallization centers on the surface of which the homogeneous structure with the increased density of interface surface is formed. The introduction of active metallurgical dust into the gypsum binders with the average size of particles 20-30 μm does not allow achieving the substantial improvement of mechanical properties that is explained by the large size of particles. It is found that the introduction of additives into gypsum compositions results in the significant change in the morphology and size of crystals.

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Keywords: gypsum binder; carbon nanotubes; crystallization centers; metallurgical dust; X-ray diffraction analysis; microstructura.**1. Introduction**

The properties of gypsum materials are mainly defined by the matrix state and structure. Different additives significantly influence the hydration process and formation of the structure of mineral binders: change the size and morphology of crystals, state of the interface surface, porosity, etc. [1-14]. The efficient use of nanodispersed additives, for example, carbon nanostructures the efficient application of which leads to deeper transformations in the structure.

The additives with nanosized particles possess a high surface energy and chemical activity, and have a stronger influence on the formation of the structure of boundary layers of mineral matrix. Thus the use of nanoparticles in polymeric matrices allows increasing the durability in up to 2 times and heat resistance by 40-50 °C due to filling the structural defects of interface boundaries of composites, forming physical and chemical bonds, and creating packing effect [15]. The application of nanosilica in concretes allows increasing durability, water and corrosion resistance due to decreasing the pores and forming the dense structure [16]. When carbon nanotubes are used in silicate matrices, the morphology of crystalline hydrate new-formations changes with the formation of calcium hydrosilicates with elevated basicity [17]. In the meantime, when ultra- and nanoadditives are used together, greater transformations in the matrix structure are achieved. In [18] we

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demonstrated that when the ultrafine metallurgical dust and carbon nanotubes are used together, the structure with elevated area of contacts in interface layers with significantly improved mechanical properties is formed due to the synergetic effect. In this regard, we assume that the efficiency of the action of carbon nanostructures will increase when introducing active ultradisperse additives with amorphous phase.

The aim of this work is the examination of the influence of ultradisperse metallurgical dust and carbon nanostructures on the structure and properties of gypsum binders.

2. 1. Materials and methods of the experiments

2.1. Materials

Gypsum of the grade G-4 produced by LLC “Prikamskaya gypsum company” (Perm) is used as a binder. The multilayer carbon nanotubes based on “Masterbatch CW2-45” by the French corporation “Arkema”, see Fig. 1a) introduced as dispersion are applied as nanostructures. The dispersion represents the granulated dispergated mixture of carbon nanotubes in the medium of carboxymethyl cellulose containing 45% of multilayer carbon nanotubes. In the process of mechanical stirring with water “Masterbatch CW2-45” transforms into the fragile dispersion with the inclusion of microsized particles, see Fig. 1b.

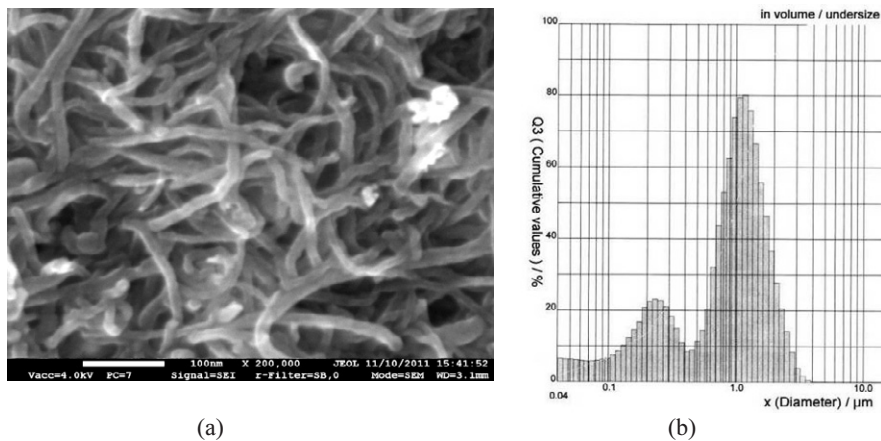


Fig. 1. Industrial samples of carbon nanotubes with grafted functional groups based on carboxymethyl cellulose of the series Masterbatch CW 2-45: (a) – general view; (b) – disperse analysis of carbon nanotubes on laser analyzer CILAS 1090 Liquid

Metallurgical (flue) dust formed in steel production process has been used as a ultradisperse additive. The additive disperse analysis demonstrated that the average size of particles is 20-30 μm (Fig. 2). The X-ray phase analysis of the metallurgical dust revealed (Fig. 3) that the most intensive peaks on the X-ray pattern correspond to iron oxide (II,III) ($d_a = 2.98; 2.54; 2.10; 1.48 \text{ \AA}$) and calcium hydroxide (Ca(OH)_2) ($d_a = 4.93; 2.63; 1.92; 1.70 \text{ \AA}$) that indicates their considerable content in the additive. There are also diffraction reflections corresponding to nickel oxide (NiO) ($d_a = 2.40; 2.10; 1.48 \text{ \AA}$). Calcium carbonate (CaCO_3) and chromium hydroxide (Cr(OH)_3) are present as additives. Besides, there is the amorphous phase in the additive.

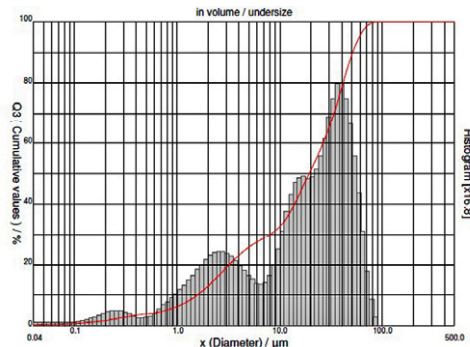


Fig. 2. Disperse analysis of of metallurgical dust on laser analyzer CILAS 1090 Liquid

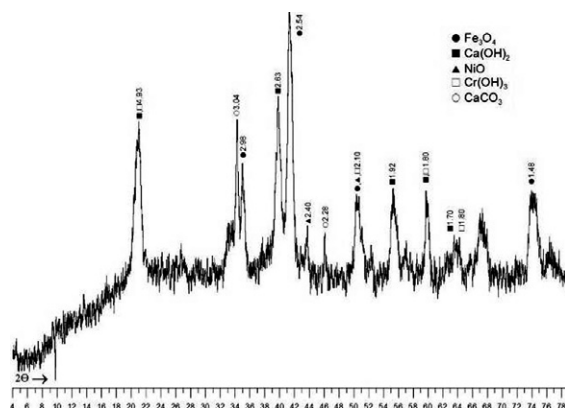


Fig. 3. X-ray diffraction pattern of metallurgical dust

2.2. Sample preparation

The ready dispersion of carbon nanotubes has been mixed with tempering water and metallurgical dust and introduced into the gypsum binder. The optimal quantity of water has been taken from the binder mass to obtain the gypsum dough with normal density. The correlation of the components of forming mixtures is given in Table 1. The components have been mixed manually within 2-2.5 minutes.

Standard steel molds with sizes 40×40×160 mm have been used to obtain the gypsum samples. The samples have been kept in the molds for 20-30 minutes with further mechanical durability tests. The samples have been stored at $T = 20\text{ }^{\circ}\text{C}$ for 28 days under normal humidity.

Table 1. Quantitative composition of gypsum specimens

Sample compositions Components	Reference sample	Sample with ultradisperse additive	Sample with nanodisperse additive	Sample with nano- and ultradisperse additives
Gypsum, %	100	99.4-99.9	99.99; 99.995; 99.999	99.395-99.895
Metallurgical dust, %	—	0.1; 0.2; 0.3; 0.4; 0.5; 0.6	—	0.2; 0.4; 0.6
Carbon nanotubes, %	—	—	0.01; 0.005; 0.001	0.005
Water-gypsum ratio, %	60	60	60	60

2.3. Test methods

The strenght tests of the samples have been carried out on hydraulic press PGM-100 with the allowed load 100 kN and loading speed 0.5 MPa/s in accordance with the standard requirements [19]. The average values calculated by the results of three successful measurements have been taken as the final test results.

The sample microstructure has been investigated with the help of microscope JSM 7500 F produced by JEOL with the accelerating voltage 4 kV and maximum magnification up to 20000 times. The X-ray phase analysis has been carried out on diffractometer DRON-2. Cobalt has been applied as an anti-cathode.

3. Investigation results and their discussion

3.1. Mechanical tests

The results of mechanical tests of the gypsum binder with the introduction of carbon nanotubes in the amount from 0 up to 0.01% after 28 days are given in Figure 4. The analysis of the results of mechanical tests demonstrates that the introduction of nanoadditive in the amount of up to 0.001% contributes to increasing the compression strength, but with further concentration elevation the gradual decrease of mechanical properties of the gypsum binder is observed. The results of mechanical tests of the samples with the introduction of nanotubes can be explained from the point of synergetics of

disperse-filled bodies [20]. The nanotubes, having high surface energy, play the role of crystallization centers with the intensive crystallization of new-formations along their surfaces. With the increase of nanotube content the number of crystallization centers goes up that contributes to the greater transformation of calcined gypsum into calcium sulfate dihydrate and results in durability elevation. However when the optimal value of nanotubes is exceeded (over 0.001%), the gradual durability decrease is observed that is connected with the binder deficiency in the boundary layers and formation of the structure with the increased porosity. In Fig. 4 you can see that when the content of nanotubes is 0.001%, the gypsum matrix porosity elevates up to 40% after 28 days, and up to 80 % after 7 days. The optimal value of the additive is in the interval between 0.001 and 0.005%.

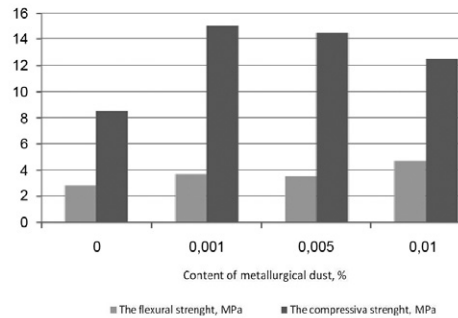


Fig. 4. Strength of the gypsum matrix with multilayer carbon nanotubes introduced

The results of mechanical tests of the gypsum binder with the introduction of metallurgical dust in the amount from 0 up to 0.6% after 28 days are given in Fig. 5. When the ultradisperse additive in the interval from 0 up to 0.4 is used no significant changes in the durability properties are observed. Probably the loss of the modifying effect is connected with a rather large size of the particles due to their aggregation. When the additive content in the gypsum matrix exceeds 0.4 %, the gradual decrease in the mechanical properties is observed. Obviously, in this case, the additive acts as an admixture on the surface of which the gypsum matrix weakens.

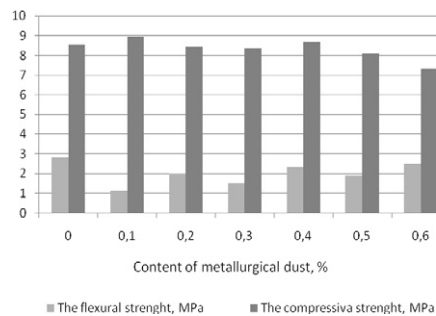


Fig. 5. Strength of the gypsum matrix with metallurgical dust introduced

The joint introduction of metallurgical dust and carbon nanotubes does not result in significant changes in durability characteristics, see Fig. 6. The values of mechanical characteristics are preserved on the level of durability indexes of the samples with nanotubes introduced. The synergetic effect, in this case, unlike the previous investigations [4], is not revealed. This can be explained by the loss of the modifying effect when using the ultradisperse additive, as a result of particle size increase.

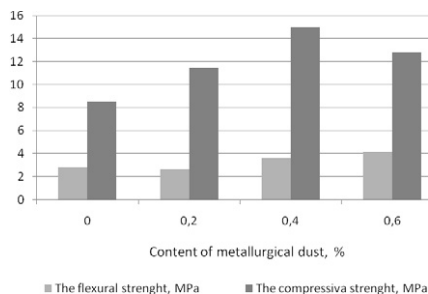


Fig. 6. Strength of gypsum matrix with the combined introduction of metallurgical dust and carbon nanotubes

The X-ray phase analysis has been carried out to find out the changes in the sample structure.

3.2. X-ray phase analysis

The X-ray diffraction analysis is applied to reveal changes in the mineralogical composition of samples. In Fig. 7a-d you can see the X-ray diffraction patterns of the samples with and without additives. The main reflections on the X-ray diffraction patterns 7 (a-d) correspond to the lines of calcium sulfate dihydrate ($d_a = 7.55-7.67$; $d_a = 4.29-4.30$; $d_a = 3.80-3.81$; $d_a = 3.07$; $d_a = 2.88$; $d_a = 2.68-2.69$), but in Fig. 7c there are also anhydrite lines with $d_a = 3.50$. Comparing the X-ray diffraction patterns we can see that when we introduce carbon nanotubes, see Fig. 7b, the intensity of reflections corresponding to calcium sulfate dihydrate ($d_a = 3.07$; 2.88) slightly increases that demonstrates the improvement of hydration process conditions. However, when we add metallurgical dust, the anhydrite line with $d_a = 3.50$ appears in the spectrum 7c which can be either connected with the interaction of gypsum and lime in the dissolving process. In X-ray diffraction pattern 7d the anhydrite line disappears that can be explained by better conditions for the binder solubility. Thus, the introduction of carbon nanotubes results in better conditions for hydration followed by more extensive transformation of gypsum binder into calcium sulfate dihydrate providing the improvement of mechanical properties of the gypsum matrix.

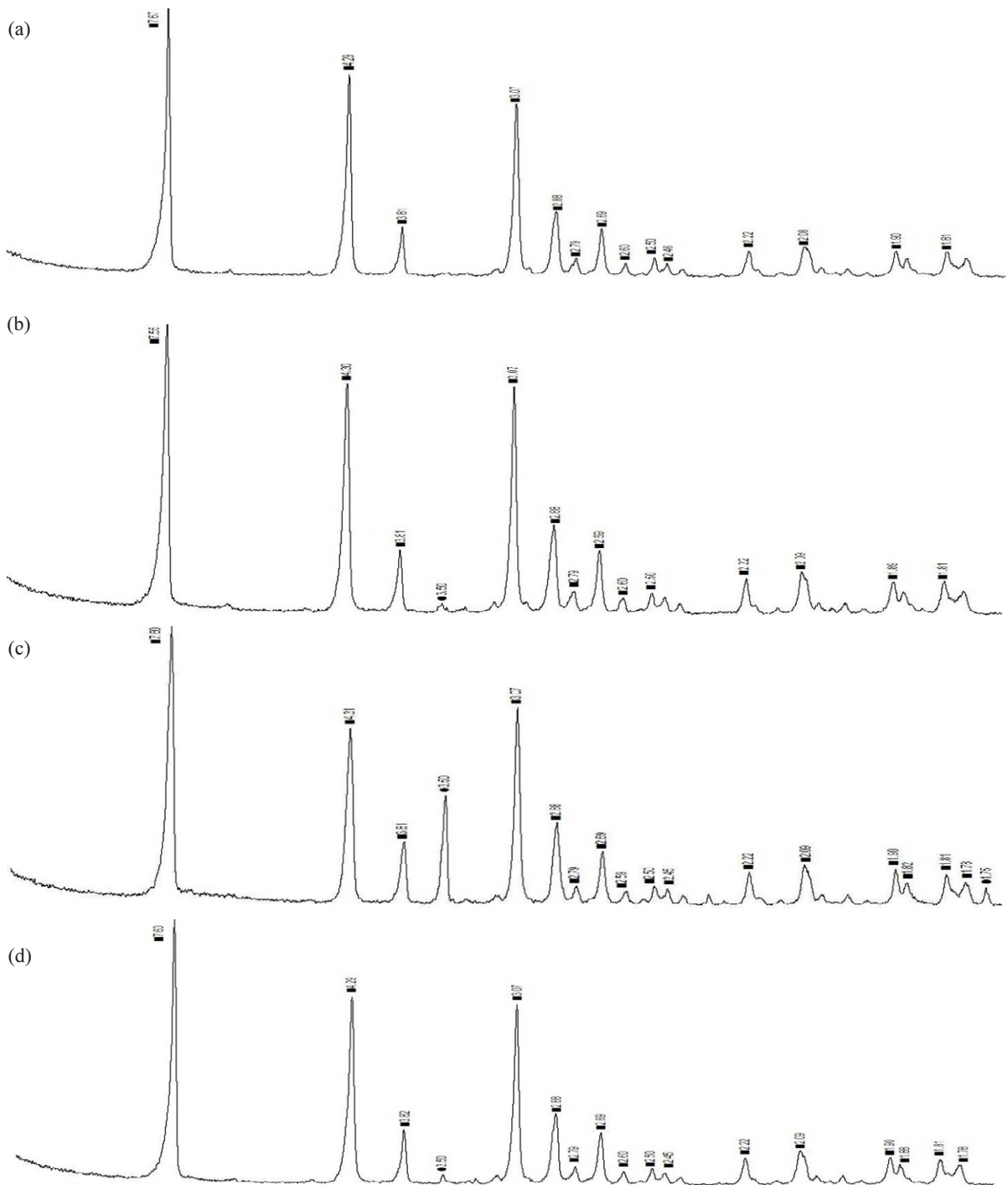


Fig. 7. X-ray diffraction pattern of gypsum matrix: (a) – reference sample; (b) – sample with the introduction of 0.005% of carbon nanotubes; (c) – sample with the introduction of metallurgical dust; (d) – sample with the introduction of metallurgical dust and carbon nanotubes (0.1% and 0.005%, respectively)

The microstructural analysis has been carried out to reveal the changes in the morphology and size of crystals.

3.3. Raster electronic microscopy

The microstructural analysis of the samples without additives demonstrates (Fig. 8a) that prismatic and lamellar crystals up to 15 μm long and up to 1-2 μm in diameter randomly spread in the matrix volume prevail in the structure of gypsum samples. In this case, the structure with the elevated porosity that results in decreased mechanical durability of the samples is formed. The ordered and homogeneous structure with larger crystals (up to 20 μm long) is formed in the gypsum matrix with carbon nanotubes added (Fig. 8b) that leads to the increased interface surface area, decreased porosity and improved physic and mechanical properties.

When the metallurgical dust is introduced (Fig. 8c), the prismatic crystals of different sizes prevail in the sample structure, block structures are also present. The joint application of dust and carbon nanotubes results in the formation of the dense structure consisting of large crystals with amorphous component on their surfaces, see Fig. 8d. Probably, when the ultradisperse additive is introduced, apart from the crystalline structure the conditions for the arrangement of amorphous structures which are formed in interface layers and additionally bind the crystalline formations

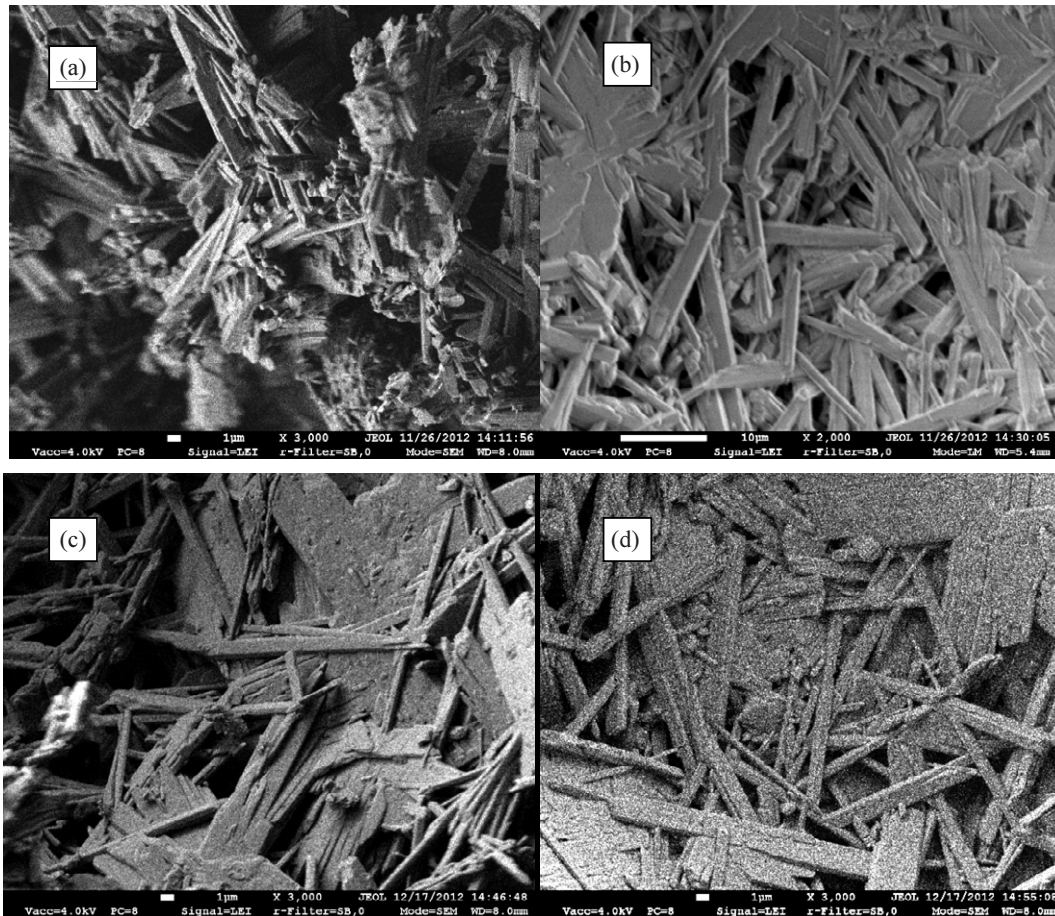


Fig. 8. Gypsum matrix microstructure: (a) – without additives; (b) – with carbon nanotubes; (c) – with metallurgical dust; (d) – with metallurgical dust and carbon nanotubes

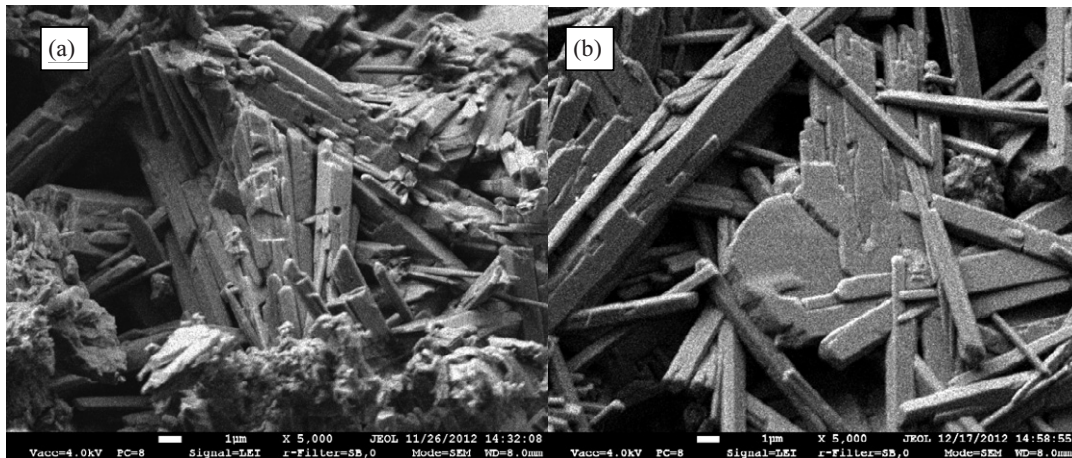


Fig. 9. Gypsum matrix microstructure ($\times 5000$): (a) – with carbon nanotubes; (b) – with metallurgical dust and carbon nanotubes

Besides, in the picture of the sample with carbon nanotubes added (Fig. 9a) we can see the packed block structure without microslots. Probably the nanotubes attract crystals due to high surface energy forming denser structures. That is, the nanotubes act as crystallization centers with more crystals of calcium sulfate dihydrate along their surface which provide the improved mechanical properties. In the picture of the sample with lime and carbon nanotubes added (Fig. 9b) we see the lamination of large crystals with dense areas of interface surface.

4. Conclusion

Carbon nanostructures act as crystallization centers on the surface of which the ordered structure with the block packing of crystals and increased density of interface surface is formed, as a result, the physic-mechanical characteristics of the gypsum matrix are improved by up to 80% at optimal additive content of 0.001 %. The introduction of active metallurgical dust does not contribute to the improvement of physic-mechanical characteristics. This is probably connected with the large sizes of the particles. Thus, the separate application of carbon nanostructures in gypsum compositions is more efficient than the joint introduction with an ultradisperse additive.

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